# ON THE GRADING OF NITROCELLULOSE MEMBRANES BY MEANS OF ETHYLENE GLYCOL.

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**DISSERTATION**

Submitted in Partial Fulfillment of the Requirements
for the Degree of Doctor of Philosophy
in the Faculty of Pure Science,
Columbia University.

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BY

ADA MARTITIA FIELD

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# ON THE GRADING OF NITROCELLULOSE MEMBRANES BY MEANS OF ETHYLENE GLYCOL.

Nitrocellulose membranes and methods of preparing them have been the subject of much investigation because of the value of such membranes in dialysis and ultrafiltration.

Ordinary films for ungraded qualitative work are easily made but the process is not so simple if one tries to produce a membrane having a certain degree of permeability,— or, having produced it, tries to so define all the factors involved that it may be reproduced by others. For the making of ordinary films a solution is prepared containing about 4 per cent of soluble nitrocellulose dissolved in some solvent which is more or less volatile and is also soluble in water. Usually the solvent is a mixture of 25 per cent by volume of 95 per cent alcohol with 75 per cent by volume of commercial ether, in which case the resulting solution is commercial "collodion." This collodion is spread thinly upon some clean, non-absorbent surface such as a glass plate, tube, or the inside of a flask, and a part of the solvent allowed to evaporate. The mold with its adherent film of collodion is then plunged into water, whereby the collodion is solidified and the film can be removed from the mold and washed free from any remaining solvent.

Several times methods for the making of "reproducible collodion membranes of graded permeability" have been reported in research journals, but only to have the next investigator locate some unrecognized variable which his predecessor had failed to control. Each new proposal has contributed, however, to the total of information regarding the effect of varying one and another factor in the preparation of membranes and regarding the methods of controlling variables.

Although Fick[1] (1855) first prepared flat nitrocellulose membranes for dialysis, and Schumacher[2] (1860) devised the useful closed sac of collodion, it was Baranetzky[3] (1872) who made the first step toward a method of varying permeability.

He noted that it was necessary to immerse the film in water before the solvent had completely evaporated if the resulting membrane was to be permeable.

Malfitano[4] found that permeability increased with increasing proportion of alcohol in the solvent mixture, but it remained for later workers to measure this important factor.

Bigelow and Gemberling[5] noted that different samples of nitrocellulose might yield membranes differing quite widely in permeability and these authors also varied permeability by varying the length of the drying time before immersing the membranes in water.

Bechhold[6] demonstrated a fourth factor which influenced permeability when he prepared a graded series of membranes by dipping filter papers into solutions which varied progressively in their nitrocellulose content, draining the papers slightly and plunging them into water. His membranes were increasingly permeable inversely to the nitrocellulose content of the acetic acid-collodion used.

Shoep,[7] and more recently Asheshov[8] and Pierce,[9] tried the effect of adding to an alcohol-ether collodion differing amounts of other solvents or diluents. Shoep used glycerol, Asheshov acetone, and Pierce ethylene glycol to increase permeability.

Walpole[10] made a study of the length of time membranes were allowed to "dry,"—or their solvents to evaporate,—before immersing in water. He found permeability varied inversely with evaporation time and recognized that "porosity" "depends primarily upon the amount of solvent remaining in the nitrocotton on the plate when it is plunged into water." Walpole also contributed an easy method of comparing membranes with each other. He found the permeability of his membranes varied with "wetness" or the ratio of water to nitrocellulose in the washed membrane. This method of testing was later substantiated by Brown,[11] by Eggerth,[12] by Nelson and Morgan[13] and by Pierce.[9]

Brown[11] developed an interesting and valuable method of grading over a range of low and moderate permeabilities. He

prepared membranes under constant conditions, washed them, dried them for 24 hours and then soaked them in alcohol-water mixtures of varying proportions and again washed in water. He found permeability varied directly with the amount of alcohol in the soaking mixture and proposed designating the volume per cent of alcohol in this mixture as the "alcohol index" of the membrane.

Eggerth [12] varied the ratio of anhydrous alcohol to anhydrous ether in the solvent mixture and prepared graded membranes of high permeability by the use of high percentages by weight of alcohol. He also noted that the addition of 10 to 20 per cent of acetic acid to his collodion yielded a stronger and more elastic but less permeable membrane, while lactic acid greatly increased permeability.

Nelson and Morgan[13] developed a technique for measuring the extent of evaporation of solvent by weighing the membrane on its glass plate previous to plunging into water. They noted that at a certain stage of evaporation the collodion solution rather suddenly "set" to a gel, and that, other conditions being constant, the weight at this point was always the same and the permeability of the washed membranes the same. They found that the permeability of their membranes could be further increased by immersing the membrane on the plate, not in pure water, but for 2 to 10 minutes each in a succession of alcohol solutions grading from 80 per cent to 10 per cent. They also noted that small amounts of moisture increased the permeability of the membranes and the fragility as well—the moisture of the breath and variations in the humidity of the room having an effect. As a basis for comparing membranes Nelson and Morgan proposed that the ratio of water in the washed membrane to the weight of the same membrane after drying be called the "grade" and be designated by the symbol "$G_w$."

$$G_w = \frac{\text{wet weight} - \text{dry weight}}{\text{dry weight}}$$

Dry weight was determined after drying overnight at 70° C.

Bjerrum[14] controlled the rate of evaporation of solvent by the use of an air current from a fan driven at constant speed.

Pierce[9] used two methods of preparing membranes. In the first of the two the nitrocellulose solution, temperature, air rate and humidity were held constant and grading of membranes brought about by varying the evaporation time. The author considered that the membranes produced were satisfactory but the apparatus was complicated and expensive. In the second method all other conditions were held constant and the grading accomplished by adding to the collodion varying percentages of ethylene glycol. Pierce also developed a comparison of membranes with each other on the basis of their permeability to distilled water under pressure and compared data by this method with the "grade" ($G_w$) as proposed by Nelson and Morgan.

The present writer, being in need of accurately graded membranes for ultrafiltration, decided upon the second method devised by Pierce as the most promising. It appeared to have several advantages. (1) The equipment required is simple and easily handled and yet provides adequately for holding constant most of the troublesome variables. (2) The rate of evaporation is very slow, giving opportunity for a thoroughly uniform texture of membrane. (3) Four membranes are prepared at one time under identical conditions and these should duplicate more closely than even the most successful individual preparations. (4) Quite a wide range of graded permeability is possible.

Attempts to duplicate Pierce's membranes were not at first successful, however. In searching for the cause of failure data were gathered which showed that his method, while providing control for known variables, introduced new ones in connection with ethylene glycol for grading and calcium chloride for drying the air. The previously known variables are noted above in connection with the literature and are fully discussed by Pierce.[9] Since the aim in the present work is to hold them constant they need not be discussed further than to enumerate them later in showing how they were controlled.

Quoting briefly from the author's description, the method in question and the principles involved are as follows:

"The essential determinant of the permeability of a membrane is the ratio of the solvent or swelling agent to the nitrocellulose in it at the moment of its immersion in water. Hence if one were to add a water-soluble, non-volatile swelling agent to alcohol-ether collodion, pour the mixture on a glass plate, and completely evaporate the alcohol and ether, the permeability of the membrane produced by immersing the plate in water should be a function of the ratio between the non-volatile swelling agent and the nitrocellulose in the collodion. . . . . Ethylene glycol was chosen as the non-volatile swelling agent, and a simple apparatus was devised to allow evaporation of the volatile solvent in dry air. . . . The solvent mixture was prepared according to the formula:

| | |
|---|---|
| Ethyl alcohol, absolute | 25 cc. |
| Ethylene glycol | 0.5 to 15 " |
| Ether, Squibb's anesthetic, to make | 100 " |

In each 100 cc. of the solvent was dissolved 1 gm. of the dry nitrocellulose."

The apparatus for evaporating the solvents consisted of a closed chamber with openings at top and bottom through which a slow current of air (10 cc. per minute) was drawn by a water aspirator. In order to dry the air thoroughly a canister of calcium chloride was fitted into each of the openings.

The findings of the present writer, as reported in the following pages, show, with regard to this method, that:

(1) Ether may perhaps be completely removed from the films at the end of 24 hours evaporation as described but the alcohol is only partly removed.

(2) The canister of calcium chloride placed below the evaporation chamber to prevent the return of moisture from the water aspirator is an agent in removing alcohol from the chamber.

(3) Other conditions being constant, the amount of alcohol retained in the membranes at the end of the evaporation period is determined by the attraction between alcohol and

ethylene glycol on the one hand as opposed to the attraction between alcohol and calcium chloride on the other. The attraction between alcohol and calcium chloride varies with the condition of the chloride.

(4) The grading of the membranes is brought about, not by the ethylene glycol alone, but by the ethylene glycol plus the alcohol which it causes to remain in the membranes.

(5) The volatility of ethylene glycol itself is not entirely negligible under the conditions of the experiment.

## EXPERIMENTAL.

### *Equipment and Methods of Work.*

As far as possible the equipment and reagents duplicated those of the previous author. The ether was Squibb's anesthetic, the absolute alcohol was manufactured by the United States Industrial Alcohol Company, the ethylene glycol by the Carbide and Carbon Chemicals Company and the collodion was du Pont's "parlodion." Two grades of calcium chloride were used: one of tested purity, calcined, granular, 8-mesh; the other technical, calcined, granular, in lumps 1 cm. or less in diameter.

As the membranes were desired larger than those made by Pierce (which were 7.5 cm. in diameter) the glass plates and evaporation chamber were larger. The plates were manufactured to order by Bausch and Lomb Company and were 9 cm. in diameter and 4 mm. thick. The surfaces were parallel, one of which was ground and the other polished. The edges were vertical and made sharp right angles with the surfaces. In use, each of 4 plates was floated on 1 kilogram of mercury in a paper-lined metal dish 12.5 cm. in diameter and 2.5 cm. deep. These dishes rested 3 cm. apart on the floor of the evaporation chamber and were levelled so that the heavy vapors of alcohol and ether might not overflow unevenly from them.

The evaporation chamber consisted of a level metal plate about 40 cm. square with a heavy tin dishpan inverted over it as a cover, the joining of cover and plate being sealed with pe-

trolatum. Openings in the center of the plate and of its cover allowed air to be drawn through, and the chamber was supported on a strong wooden box, open at one side, so that containers for calcium chloride could be attached below the chamber. The opening in the cover was 12 cm. in diameter and over it an inverted funnel was soldered. As a baffle to help distribute the incoming current of air evenly this 12 cm. opening from funnel to chamber was screened with fine wire gauze and a layer of muslin. A straight calcium chloride tube 20 cm. long was attached by rubber connections to the tube of the funnel and hung downward. In all experiments where the air rate was 40 liters or more a day this drying tube was supplemented by an additional column of calcium chloride 45 cm. long. Only the pure 8-mesh chloride was used in these tubes through which the air passed when entering the chamber. The exit opening in the floor of the chamber was 42 mm. in diameter and various sizes of tubes were fastened into it for the various experiments, as will be described later.

The inside dimensions of the closed chamber were as follows: bottom diameter, 38 cm.; top diameter, 29 cm.; height, 13.4 cm. The capacity was therefore about 12 liters, and is greater than would be desirable if the slow (22 liters a day) current of air was employed exclusively. Twelve liters of air, necessarily enclosed at room humidity, would be expected to cause variation in permeability of membranes and probably did cause some variation. The error from this source was not great enough to be taken into account in the present investigation, however, as was shown by a test with air purposely rendered humid and also by keeping a close record of approximate air conditions throughout the work and noting the character of membranes obtained.

Air was drawn through the evaporation chamber by an aspirator bottle graduated in liters or, when the rate exceeded 40 liters a day, by a water pump, the rate of which was regulated by capillary tubing and a safety valve.

Since the surface of 9 cm. plates is very nearly one and a half times that of the 7.5 cm. plates used by Pierce, a 6 cc.

pipette for measuring collodion replaced his of 4 cc. About 1¼ minutes were required to measure the collodion onto the four plates and close the chamber.

The temperature was held as nearly as possible at 20° ± 1° C., as recorded by a maximum and minimum thermometer placed in contact with the evaporation chamber. In all the later experiments the chamber was protected from drafts and sudden changes in room temperature by being covered first with a large corrugated paper box and then with blankets. Variations in temperature and also in rate of air flow seemed to have a more pronounced effect toward the end of the evaporation period and consequently the preparation of membranes was begun in the late afternoon so that the later stages could be kept under observation the next day. Day temperatures were usually kept at 20° ± 0.5° C. Wherever, in the tables following, temperatures higher than 21° or lower than 19° appear they had extended over only a few hours. Such variations over the whole 24 hour period would affect the membrane noticeably.

Distilled water was used in washing membranes because it was found to give less variable results than tap water.

Summarizing those factors in membrane preparation which, as noted above, have been found by previous investigators to affect permeability, and listing together with them the means employed to control them in the present work, we have the following:

Factor (1): kind of nitrocellulose. Probably kept constant by the use of a single, well mixed sample of "parlodion."

Factor (2): percentage of nitrocellulose in solution. One per cent solutions used throughout.

Factor (3): character of solvent. Alcohol-ether mixture in which the volume per cent of alcohol was constant and the ether nearly so.

Factor (4): other liquids added to solvent mixture. Ethylene glycol in volume percentages of 2, 3, 4, and 5, each concentration being constant through a series of tests.

Factor (5): temperature. Kept as nearly as possible at 20° C.

Factor (6): rate of air movement over membranes. Kept at 22 ± 1 liters for the evaporation period except when being used as a variable. This rate was about 1.5 times that used by Pierce and was chosen because the membrane surface, and hence the volume of solvent to be removed, was nearly 1.5 times the membrane surface in his work.

Factor (7): drying time. Constant at 24 hours or at 10 hours.

Factor (8): humidity. (a) Humidity in collodion solution. The parlodion was air dried for two days and dried over solid sodium hydroxide in a desiccator for three days; alcohol was "absolute"; ether was of reasonably constant moisture content (Pierce[9]); one sample of ethylene glycol of specific gravity 1.1172 at 15° C. was used throughout. (b) Humidity on plates. Plates were kept in cleaning mixture or in water when not in use and were rinsed, thoroughly dried with a clean towel and allowed to stand for about five minutes before using. (c) Humidity in air in which membranes were dried. Air was passed through calcium chloride of high absorptive power. (d) Humidity in air of room. Not controlled but effect negligible under conditions existing in present work, as stated above. Not negligible where the highest precision is required in reproducing membranes.

The factors studied as variables in the present investigation were: (1) the effect produced upon membranes by wide variations in air rate; (2) the effect produced by the kind, amount and accessibility of the calcium chloride to which the alcohol vapor was exposed either in the evaporation chamber or below it.

Comparison of all membranes with each other was made on the basis of wet weights and "$G_w$." Wet weights were obtained by blotting off surface moisture with smooth filter paper (Whatman No. 1) and quickly enclosing the film in a weighing bottle. Drying was done in an air oven at 100° C. over night.

In addition to wet weights, all the later experiments included "weight before washing" for one membrane in each set. This was found in the following way. On opening the chamber at the end of the evaporation period one membrane, always in the same position in the chamber, was quickly covered with a 9-cm. watch glass and left in place while the other three were removed to distilled water at 20° C. The covered one was then weighed to the nearest milligram and plunged into the water. The air under the watch glass lifted it so that the membrane was usually uninjured. Nelson and Morgan[13] state that membranes which were weighed uncovered lost at a rate of about 50 mg. per minute during the weighing, and the writer found similar losses. When covered, however, very little loss of weight occurred on the balance and the wet weight of this previously weighed film differed little from that of others of the same lot. Membranes weighed uncovered, unless they had been allowed to evaporate so thoroughly that alcohol was practically no longer being given off, had wet weights ranging from 26 to 100 mg. lower than those of previously unweighed films of the same lot.

The four membranes were numbered according to their places in the evaporation chamber so that any differences in temperature on different sides of the chamber could be detected. Unless stated to the contrary each wet weight recorded in the tables which follow is the average for three of the four membranes in a set and frequently of the four.

## RESULTS

The new variable factors introduced into membrane making by the use of ethylene glycol for grading and calcium chloride as air drying agent are due to properties which may be summed up by saying that ethylene glycol readily absorbs alcohol and water, while calcium chloride absorbs all three. In order to examine these properties in a less complex situation than exists in a collodion membrane some simple experiments were made in two-liter Sheibler desiccators.

(1) *Desiccator Experiments with Ethylene Glycol.*

The glycol, in 5 cc. portions, was placed quickly in crystallizing dishes 5 cm. in diameter and 3 cm. deep. Each was covered with a watch glass for weighing and was then placed on a wire gauze support in the desiccator. Absolute alcohol or

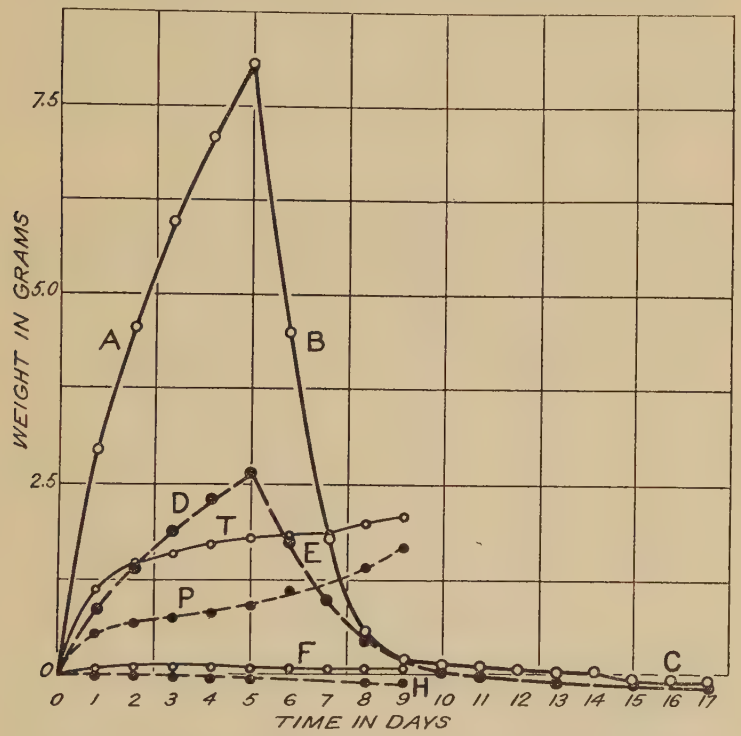


Fig. 1. Weight changes in ethylene glycol when enclosed in a desiccator under various conditions. Data from Table I.

A. With a dish of alcohol only.
B. With alcohol dish removed from "A" and pure calcium chloride introduced.
C. With calcium chloride in "B" replaced by fresh chloride.
D. With a dish of water only.
E. With water dish removed from "D" and pure calcium chloride introduced.
F. With pure calcium chloride which had previously absorbed 5 cc. of alcohol.
H. With pure calcium chloride only.
P. With alcohol and pure calcium chloride.
T. With alcohol and technical calcium chloride.

water, as the case might be, was placed in a similar dish 4 cm. from the dish of glycol, while the calcium chloride, when used, was about 8 cm. below on the bottom of the desiccator. The changes in weight of the ethylene glycol under various conditions are summarized in Table I and Figure 1. These values are uncorrected for evaporation of ethylene glycol itself and are somewhat inaccurate, both because of temperature variations and on account of opening the desiccator daily for weighing the dish of glycol, but they indicate clearly the general relationships involved.

TABLE I.

**Weight Changes of Ethylene Glycol when Exposed in a Closed Space to Room Atmosphere, to Calcium Chloride and to the Vapors of Alcohol and of Water.**

Temperature about 20° C. but not constant.

| No. of Experiment | Ethylene glycol, 5 cc., in 5-cm. dish placed in 2-liter desiccator with: Calcium chloride* P=Pure T=Technical *gms.* | Absolute alcohol in 5 cm. dish *cc.* | Water in 5 cm. dish *cc.* | Changes in weight of glycol in periods of: 24 hrs. *gms.* | 48 hrs. *gms.* | 72 hrs. *gms.* | 5 days *gms.* |
|---|---|---|---|---|---|---|---|
| I. Glycol enclosed alone: (1a) on a damp day, (1b) on a dry day. | | | | | | | |
| 1a | None | None | None | +0.121 | +0.152 | +0.166 | +0.17 |
| 1b | None | None | None | +0.027 | +0.035 | +0.040 | |
| II. Glycol enclosed with calcium chloride. | | | | | | | |
| 2 | P. 10 gms. in a 4 cm. weighing bottle | None | None | –0.004 | –0.005 | –0.009 | –0.02 |
| 3 | P. 50 gms. | None | None | –0.009 | –0.019 | –0.030 | –0.05 |
| III. Glycol enclosed with absolute alcohol. | | | | | | | |
| 4 | None | 50 | None | +2.93 | +4.59 | +6.00 | +8.08 |
| IV. Glycol dish removed after 5 days from (III) above and placed in a fresh desiccator. | | | | | | | |
| 5 | P. 50 gms. | None | None | –3.53 | –6.26 | –7.52 | –7.95 |
| V. Glycol dish from (IV) above again removed to fresh desiccator when, after 9 days, it was losing wt. at the rate of about 0.011 gms. per day. | | | | | | | |
| 6 | P. 50 gms. | None | None | –0.064 | –0.086 | –0.106 | –0.14 |

TABLE I—(continued)

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| | VI. Glycol enclosed with both alcohol and calcium chloride. | | | | | | |
| 7 | P. 10 gms. in 4 cm. bottle | 50 | None | +1.32 | +2.02 | +2.69 | +3.86 |
| 8 | P. 50 gms. | 50 | None | +0.55 | +0.68 | +0.75 | +0.93 |
| 9 | T. 50 gms. | 50 | None | +1.12 | +1.42 | +1.60 | +1.82 |
| | VII. Glycol enclosed with calcium chloride which had previously absorbed 5 cc. of alcohol. | | | | | | |
| 10 | P. 50 gms. | None | None | +0.097 | +0.114 | +0.112 | +0.09 |
| | VIII. Glycol enclosed with a dish of water. | | | | | | |
| 11 | None | None | 10 | +0.83 | +1.41 | +1.90 | +2.70 |
| | IX. Glycol dish removed, after 5 days, from (VIII) above and placed in fresh desiccator. | | | | | | |
| 12 | P. 50 gms. | None | None | –0.95 | –1.70 | –2.23 | –2.64 |
| | X. Glycol enclosed with both water and calcium chloride. | | | | | | |
| 13 | P. 50 gms. | None | 10 | +0.42 | +0.67 | +0.86 | +1.04 |
| 14 | T. 50 gms. | None | 10 | +0.47 | +0.80 | +1.02 | +1.29 |
| | XI. Glycol enclosed with calcium chloride which had previously absorbed 5 cc. of water. | | | | | | |
| 15 | P. 50 gms. | None | None | 0.000 | –0.003 | –0.011 | –0.035 |

* Except where noted the calcium chloride was spread on bottom of desiccator.

When the glycol was enclosed alone in an air dry desiccator on a very damp day it gained 0.121 gms. in 24 hours while a similar test started on a comparatively dry day gained only 0.027 gms. in that time. When 50 gms. of pure calcined calcium chloride was placed in the desiccator before introducing the dish of ethylene glycol there was a loss in weight lasting as long as the experiment was carried on,—in one case for 25 days—this loss averaging about 0.01 gm. per day after the first two or three days. No other explanation seems possible except to consider that the glycol was evaporating and the vapor being absorbed by the calcium chloride for if the loss was due to traces of impurity in the glycol the rate would be expected to drop after a short time. This loss of 0.01 gm. per day is in quiet air and from a sur-

face 5 cm. in diameter, whereas the surface of a membrane 7.5 cm. in diameter is more than twice as great, and that of a membrane 9 cm. in diameter more than three times as great. Even supposing the loss of glycol from the membrane in 24 hours was not hastened by the slow current of air through the evaporation chamber or by the evaporation of the alcohol and ether (both unlikely suppositions) this would mean a loss of about 0.02 and 0.03 gm. per membrane respectively. Such a loss might be almost negligible for membranes high in ethylene glycol, but not for those of lower grade. It may account for the fact that in the graded series of membranes reported by Pierce[9] we find, instead of a perfect gradation, values of "$G_w$" slightly too low in the case of the one and two per cent membranes and slightly too high for all above four per cent.

When ethylene glycol was enclosed in a desiccator along with a dish of alcohol the glycol gained 2.93 gms. in 24 hours and 8.08 gms. in 5 days, but on being removed to a desiccator containing 50 gms. of pure calcium chloride it lost weight rapidly,—3.53 gms. in 24 hours, and 7.95 gms. in 5 days. After 9 days the rate of loss became practically constant at about 0.011 gms. per day. The alcohol was not all removed, however, for when the dish of ethylene glycol was transferred to a desiccator containing fresh calcium chloride the loss was increased to 0.06 gms. for the first 24 hours and 0.14 for five days. (See Curves A, B, and C, Figure 1.)

If, in the above experiment, 50 gms. of technical calcium chloride is enclosed along with the alcohol and the glycol the latter gains in weight much more slowly than before,— 1.12 gms. the first day and 1.8 in 5 days. By substituting pure for technical chloride the rate is still further reduced and becomes 0.55 for 24 hours and 0.93 for 5 days.

Ethylene glycol may absorb alcohol from calcium chloride as well as the reverse. When a dish of glycol was placed in a desiccator above 50 gms. of pure chloride which had previously absorbed 5 cc. of alcohol the glycol gained 0.097 gms. the first day and 0.114 gms. in two days. By the third day equilibrium had been so nearly reached that the evapora-

tion of the glycol became apparent and loss of weight began. The system alcohol-ethylene glycol-calcium chloride tends to a state of equilibrium in which the alcohol is distributed between the other two components and either glycol or calcium chloride may absorb alcohol from the other until this point is reached.

Desiccator tests in which water took the place of alcohol show generally similar but smaller changes. (See Curves D and E, Figure 1). When the dish of ethylene glycol was placed in a desiccator with 50 gms. of calcium chloride which had previously absorbed 5 cc. of water there was no change of weight the first day and then a loss began. Probably a slight absorption of moisture balanced the loss from evaporation of the glycol at first.

### (2) *Experiments with Membranes.*

The relationships of ethylene glycol, alcohol and calcium chloride which have been found in the desiccator experiments appear also in the preparation of membranes.

Membranes were prepared from only a short series of nitrocellulose solutions,—those containing 2, 3, 4, and 5 per cent of ethylene glycol. This group, as reported by Pierce,[9] most nearly conforms to his expected values as expressed in the ratio

$$\frac{\text{wet weight} - \text{dry weight}}{\text{dry weight}} = G_w$$

and might therefore be considered as most typical of the method. It was thought that more information could be obtained by an intensive study of this group than by using a wider range less intensively.

In the 6 cc. of solution required for the making of a membrane 9 cm. in diameter the weights of the components would be as follows:

| Nitrocellulose (1%) | Alcohol (25% by volume) | Ether (About 70% by vol.) | Ethylene Glycol 2% | 3% | 4% | 5% |
|---|---|---|---|---|---|---|
| 0.060 gm. | 1.18 gm. | 3 gms. | 0.134 | 0.201 | 0.268 | 0.335 |

This would give as the weights of the relatively non-volatile ingredients,—nitrocellulose plus ethylene glycol,—0.194, 0.261, 0.328, and 0.395 gms. respectively for the 2, 3, 4, and 5 per cent membranes. If, therefore, the volatile ingredients,—alcohol and ether,—were completely evaporated and there was no loss of ethylene glycol in the process, the above weights should accord with the weights of the corresponding membranes on the glass plates when they were removed from the evaporation chamber and previous to washing. When the above weights are compared, however, with the weights experimentally determined and reported in Tables III to VII it is clear that neither of the above conditions is fulfilled. In all cases where the "$G_w$" equals or exceeds the percentage of ethylene glycol in the collodion used the weight of the membrane before washing is greater than the weight of its non-volatile components as given above. Such membranes smelled of alcohol and lost weight rapidly in air. In a few cases, however, membranes gained weight on the balance if weighed uncovered. The third entry in Table III, column 7, is for such a membrane but its weight was 0.161 gms. while the "expected" weight for a 2 per cent membrane as given above is 0.194 gms. On the highly improbable supposition that all the alcohol had been removed from this membrane it shows a loss of 0.033 gms. of ethylene glycol. The wet weight of this membrane was 0.103 and $G_w$ was 0.8, while the wet weight required to give a $G_w$ of 2 would be about 0.174 gms.

Turning now to a consideration of the volatile ingredients, the alcohol and ether, and the space required for their complete volatilization, we find the following: The collodion for the four membranes prepared at one time contains $4 \times 1.18 = 4.72$ gms. of alcohol and $4 \times 3 = 12$ gms. ether. For vaporizing completely at their normal vapor tension for 20° C. this amount of ether would require a space of about 9 liters and the alcohol about 40 liters. While, therefore, the ether could evaporate completely in a 12-liter chamber the alcohol would require about 28 liters of additional air. But the vapor tension of alcohol is lowered by the presence of

ethylene glycol and probably by the other components of the nitrocellulose solution as well. In the experiments in desiccators recorded above it was found that a dish of alcohol was empty after 24 hours in a desiccator with 50 gms. of calcium chloride but when the dish contained also an amount of ethylene glycol equal to about half the volume of alcohol the rate of evaporation was lower and when the proportion of glycol became greater the alcohol evaporated still more slowly. A total volume of more than 40 liters of air would be required therefore for the complete removal of alcohol from the membranes. Experimentally this is shown by the data summarized in Table II. Passing an air volume of 43 liters through the

TABLE II.

**Effect Produced upon Membranes by Varying the Air Rate.**

Temperature=about 20° C.
Diameter of exit from chamber=7 mm. or less.

| No. of experiment | Ethylene glycol in collodion *per cent* | Drying time *hours* | Volume of air used *liters* | Wet weight of membranes (W) (Aver. of 3 or 4) *grams* | Dry weight of membranes (D) *grams* | Gw $\left\{\frac{W-D}{D}\right\}$ |
|---|---|---|---|---|---|---|
| 1 | 3 | 24 | 43 | 0.250* | 0.058 | 3.3 |
| 2 | 3 | 24 | 860 | 0.147 | 0.055 | 1.7 |
| 3 | 4 | 24 | 43 | 0.355* | 0.059 | 5.0 |
| 4 | 4 | 24 | 860 | 0.189 | 0.055 | 2.4 |
| 5 | 5 | 28 | 50 | 0.356 | 0.059 | 5.0 |
| 6 | 5 | 24 | 860 | 0.233* | 0.055 | 3.2 |

* Averages for two membranes only.

evaporation chamber failed to remove the volatile components sufficiently to give a value of $G_w$ as low as the ethylene glycol content of the 3, 4, and 5 per cent solutions used. When the rate was increased to 150 or more liters a day sufficiently low values of $G_w$ were obtained but the membranes had a papery feel and were of poor quality. Some agent more efficient than air in removing alcohol is required, apparently.

The effect of placing varying small amounts of pure calcined calcium chloride near the floor in the center of the evaporation chamber was next tried. As may be seen in Table III,

TABLE III.

**Effect Produced upon Membranes when Varying Amounts of Calcium Chloride were Placed inside of Evaporation Chamber.**

Ethylene glycol in collodion=2%
Dry weight of membranes (D)=0.057 to 0.059 gms.

| No. of experiment | Weight of calcium chloride *grams* | Diameter of exit tube *millimeters* | Drying time *hours* | Temperature *Deg. C.* | Volume of air *liters* | Wt. of one membrane before washing *grams* | Wet wts. of membranes (W) (Aver. of 3 or 4) *grams* | $G_w \left\{\frac{W-D}{D}\right\}$ |
|---|---|---|---|---|---|---|---|---|
| 7 | None | 7 | 24 | 20–21 | 22 | 0.393† | 0.367 | 5.3 |
| 8 | 2 | 2 | 24 | 21–24 | 21 | 0.203† | 0.135 | 1.3 |
| 9 | 10 | 2 | 24 | 16–22 | 21 | 0.161† | 0.103 | 0.8 |
| 10 | None | 20 | 10 | 20±.5 | 23 | 0.520 | 0.379* | 5.4 |
| 11 | 0.5 | 20 | 10 | 20±.5 | 22 | 0.426 | 0.260 | 3.5 |
| 12 | 1 | 20 | 10 | 20±.8 | 22 | 0.408 | 0.238 | 3.1 |
| 13 | 1.9 | 20 | 10 | 20±.5 | 22 | 0.262 | 0.160 | 1.7 |

† Weighed uncovered. * One membrane only.

membranes varying in $G_w$ from 0.8 to 5.3 were prepared from the same sample of collodion (containing 2 per cent of ethylene glycol) when the evaporation period was the usual one of 24 hours and the volume of air used was about 22 liters. When the period was shortened to 10 hours in order to control the temperature accurately the corresponding variations in $G_w$ were from 1.7 to 5.4. Even so small an amount of calcium chloride as 0.5 gm. had a marked effect, the $G_w$ being lowered about a third thereby.

Up to this time the container for chloride which was attached to the outlet in the floor of the evaporation chamber was an ordinary calcium chloride tube of medium size and the opening to the chamber was small. The charge of chloride was used repeatedly and changed only when it appeared moist. For the experiments which follow, either Gooch funnels or metal cylinders for holding the chloride were attached to the bottom of the 42 mm. outlet tube or slipped inside of it. Except where noted to the contrary these containers were freshly charged for each test with about 20 gms. of calcium chloride. By this arrangement it was possible to study the effect of variations in the diameter of the opening between the chamber

TABLE IV.

**Effect Produced upon Membranes by Size of Exit from Evaporation Chamber to Calcium Chloride Container**

Time=24 hours.
Dry weight of membranes (D)=0.057—0.059

| No. of experiment | Ethylene glycol in collodion *per cent* | Diameter of exit *millimeters* | Distance of chloride below floor *centimeters* | Temperature *Deg. C.* | Volume of air *liters* | Wt. of one membrane before washing *grams* | Wet wt. (W) of membranes (Aver. of 3 or 4) *grams* | Gw $\left\{\frac{W-D}{D}\right\}$ |
|---|---|---|---|---|---|---|---|---|
| 7 | 2 | 7 | 12 | 20–21 | 22 | 0.393† | 0.367 | 5.3 |
| 14 | 2 | 20 | 1 | 20 | 21 | 0.441 | 0.292* | 4.0 |
| 15 | 2 | 35 | 1 | 19.5–22 | 23 | 0.270 | 0.172 | 2.0 |
| 16 | 2 | 40 | 1 | 17.5–20.5 | 22 | 0.226 | 0.145 | 1.5 |
| 17 | 3 | 31 | 1 | 20–21 | 23 | 0.403 | 0.262* | 3.4 |
| 18 | 3 | 35 | 1 | 20–21.5 | 23 | 0.354 | 0.231 | 3.0 |
| 19 | 3 | 40 | 1 | 20–21.5 | 22 | 0.311 | 0.197 | 2.5 |
| 20 | 4 | 35 | 1 | 20–22 | 22 | 0.440 | 0.295 | 4.1 |
| 21 | 4 | 40 | 1 | 19.5–21 | 21 | 0.400 | 0.255 | 3.5 |
| 22 | 5 | 35 | 1 | 19.5–21 | 22 | 0.584 | 0.398 | 5.7 |
| 23 | 5 | 40 | 1 | 20–21 | 21 | 0.499 | 0.334 | 4.9 |

† Weighed uncovered. The wet weight of this membrane (rejected) was 0.267.
* Average for two membranes only.

and the chloride. Table IV and Figures 2 and 3 show that the $G_w$ of membranes decreases progressively with increase in diameter of opening. With openings varying in diameter from 7 to 40 mm. the $G_w$ of membranes made from collodion which contained 2 per cent of ethylene glycol varied from 5.3 to 1.5, while diameters of 31 and 40 mm. gave respectively $G_w$ values of 3.4 and 2.5 for membranes made from 3 per cent collodion.

The distance from the floor of the chamber to the surface of the calcium chloride also makes a difference. Table V shows that while variations of one centimeter or a little more may be negligible, a variation of 6.5 cm. changes the $G_w$ of 4 per cent membranes from 3.5, when pure calcium chloride is one cm. below the floor, to 3.9 or 4.0 when the distance is

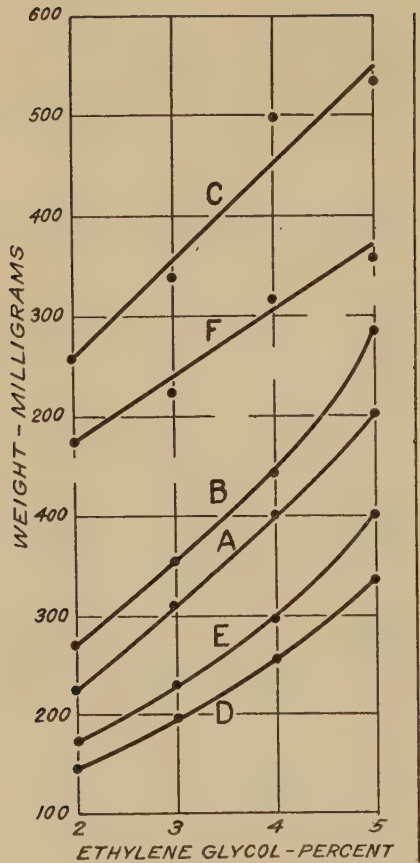


Fig. 2

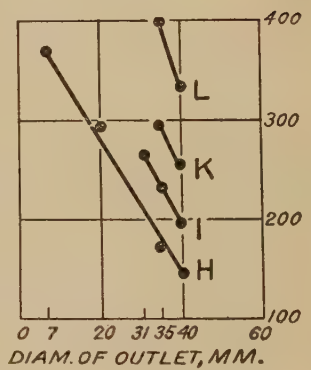


Fig. 3

Fig. 2. Membrane weights in relationship to percentage of ethylene glycol in collodion used. Data from Tables IV and (averages) VI.

(1) When diameter of outlet from evaporation chamber was 40 mm. and pure calcium chloride was absorbing agent.
A.—Weights before washing; D.—wet weights.

(2) When diameter was 35 mm. and pure calcium chloride used.
B.—Weights before washing; E.—wet weights.

(3) When diameter was 40 mm. and technical calcium chloride used.
C.—Weights before washing; F.—wet weights.

Fig. 3. Wet weights of membranes in relationship to diameter of outlet from evaporation chamber. Percentage of ethylene glycol in collodion used: H=2%, I=3%, K=4%, L=5%. Data from Table IV.

TABLE V.

**Effect Produced upon Membrane by Distance from Floor of Evaporation Chamber to Surface of Calcium Chloride.**

Drying time=24 hours.
Diameter of exit=40 mm.
Dry weight of membranes (D)=0.057 to 0.060 gms.

| No. of experiment | Ethylene glycol in collodion *per cent* | Distance of chloride below floor *centimeters* | Temperature *Deg. C.* | Volume of air *liters* | Wt. of one membrane before washing *grams* | Wet wts. (W) of membranes (Aver. of 3 or 4) *grams* | Gw $\left\{\frac{W-D}{D}\right\}$ |
|---|---|---|---|---|---|---|---|
| 21 P* | 4 | 1 | 19.5–21 | 21 | 0.400 | 0.255 | 3.5 |
| 24 P | 4 | 7.5 | 19–21 | 21 | 0.432 | 0.280 | 3.9 |
| 25 P | 4 | 7.5 | 18–20.5 | 22 | 0.437 | 0.285 | 4.0 |
| 26 P | 4 | 9.0 | 19–21 | 22 | 0.416 | 0.288 | 4.1 |
| 27 T† | 4 | 1 | 19.5–20.5 | 23 | 0.498 | 0.314 | 4.2 |
| 28 T | 4 | 7.5 | 19.5–20.5 | 22 | 0.511 | 0.341 | 4.7 |

* P=pure calcium chloride.

† T=technical calcium chloride.

increased to 7.5 cm. When technical calcium chloride is substituted for the pure the effect of the same change in distance is to change the $G_w$ from 4.2 to 4.7.

As previously stated the absorbing agent used above the chamber was in all cases pure calcium chloride and unless indicated to the contrary this was employed below the chamber as well. Table VI shows that the differences produced by substituting a good quality of technical chloride are considerable. The values of $G_w$ are from 0.1 to 0.8 higher with the technical chloride. Not only is the technical chloride a poorer absorbent for alcohol but it appears to be more variable, as may be seen in Figure 2, curves C and F, as compared with the corresponding ones A and D for pure chloride.

In Table VII data are assembled showing the effect of repeated use of the same charge of calcium chloride below the evaporation chamber. Six tests were made in which pure chloride was used at a distance of 7.5 cm. below the floor. In two of these the chloride was used for the first time and the values of $G_w$ obtained were 4.0 and 3.9. When the chloride

TABLE VI.

**Effect Produced upon Membranes by Quality of Calcium Chloride Used below Evaporation Chamber.**

Drying time=24 hours.
Diameter of exit=40 mm.
Dry weight of membranes (D)=0.057 to 0.061 gms.

| No. of experiment | Quality of calcium chloride | Ethylene glycol in collodion *per cent* | Distance of chloride below floor *centimeters* | Temperature *Deg. C.* | Volume of air *liters* | Wt. of one membrane before washing *grams* | Wet wts. (W) of membranes (Aver. of 3 or 4) *grams* | Gw $\left\{\frac{W-D}{D}\right\}$ |
|---|---|---|---|---|---|---|---|---|
| 16 | Pure | 2 | 1 | 17.5–20.5 | 22 | 0.226 | 0.145 | 1.5 |
| 29 | Tech. | 2 | 1 | 19.5–20.5 | 22 | 0.262 | 0.174 | 1.8 |
| 30 | Tech. | 2 | 1 | 19.5–21.5 | 23 | 0.254 | 0.173 | 1.8 |
| 19 | Pure | 3 | 1 | 20–21.5 | 22 | 0.311 | 0.197 | 2.5 |
| 31 | Tech. | 3 | 1 | 19.5–20.5 | 22 | 0.346 | 0.232* | 3.0 |
| 32 | Tech. | 3 | 1 | 20–21 | 22 | 0.335 | 0.219 | 2.7 |
| 33 | Tech. | 3 | 1 | 19.5–21.5 | 22 | 0.343 | 0.221* | 2.8 |
| 34 | Tech. | 3 | 1 | 20–21 | 22 | 0.329 | 0.214 | 2.6 |
| 21 | Pure | 4 | 1 | 19.5–21 | 21 | 0.400 | 0.255 | 3.5 |
| 27 | Tech. | 4 | 1 | 19.5–20.5 | 23 | 0.498 | 0.314 | 4.2 |
| 24 | Pure | 4 | 7.5 | 19–21 | 21 | 0.432 | 0.280 | 3.9 |
| 25 | Pure | 4 | 7.5 | 18–20.5 | 22 | 0.437 | 0.285 | 4.0 |
| 28 | Tech. | 4 | 7.5 | 19.5–20.5 | 22 | 0.511 | 0.341 | 4.7 |
| 23 | Pure | 5 | 1 | 20–21 | 21 | 0.499 | 0.334 | 4.9 |
| 35 | Tech. | 5 | 1 | 20–21 | 23 | 0.532 | 0.356 | 5.1 |

* Average for two membranes only.

had been previously used from one to three times the values of $G_w$ were 3.8, 4.0, 3.9, and 4.0. Two tests, involving a first and second use of the absorbing agent, were made at a distance of 9 cm. below the floor. These gave $G_w$ values of 4.1 and 4.0. Corresponding tests with a first and sixth use of technical chloride at 7.5 cm. below the floor gave values of 4.7 and 5.1 respectively. In all of these the collodion was the same,—containing 4 per cent ethylene glycol. Smaller variation was shown in other cases where 2 and 3 per cent glycol-collodion was used with technical chloride. It seems therefore that using the same (40-50 gm.) charge of chloride for

## TABLE VII.

### Effect Produced upon Membranes by Repeated Use of the Same Charge of Calcium Chloride below the Evaporation Chamber.

Drying time=24 hours.
Volume of air=21 to 23 liters.
Dry weight of membranes (D)=0.057 to 0.061 gms.

| No. of experiment | No. of times calcium chloride was used | Ethylene glycol in collodion | Diameter of exit | Distance of chloride below floor | Temperature | Wt. of one membrane before washing | Wet wts. (W) of membranes (Aver. of 3 or 4) | Gw $\left\{\frac{W-D}{D}\right\}$ |
|---|---|---|---|---|---|---|---|---|
| | | *per cent* | *millimeters* | *centimeters* | *Deg. C.* | *grams* | *grams* | |
| 36 T* | 3rd | 2 | 40 | 7.5 | 19.5–20.5 | 0.243 | 0.149 | 1.6 |
| 37 T | 4th | 2 | 40 | 7.5 | 19–20 | 0.267 | 0.158 | 1.7 |
| 38 T | 4th | 2 | 40 | 7.5 | 19.5–20.5 | 0.253 | 0.161 | 1.8 |
| 39 T | 1st | 2 | 42 | 7.5 | 17–20 | 0.237 | 0.150 | 1.6 |
| 40 T | 2nd | 2 | 42 | 7.5 | 19.5–20.5 | 0.248 | 0.158 | 1.7 |
| 41 T | 3rd | 2 | 42 | 7.5 | 20–21 | 0.244 | 0.158 | 1.7 |
| 42 T | 1st | 3 | 40 | 1.5 | 18.5–20 | 0.342 | 0.211 | 2.6 |
| 43 T | 2nd | 3 | 40 | 1.5 | 18.5–20 | 0.339 | 0.210 | 2.6 |
| 44 T | 3rd | 3 | 40 | 1.5 | 19.5–20.5 | 0.322 | 0.205 | 2.5 |
| 45 T | 1st | 3 | 42 | 7.5 | 19.5–20.5 | 0.342 | 0.216 | 2.7 |
| 46 T | 2nd | 3 | 42 | 7.5 | 19.5–20.5 | 0.352 | 0.225† | 2.8 |
| 47 T | 3rd | 3 | 42 | 7.5 | 17–20.5 | 0.363 | 0.232‡ | 3.0 |
| 48 T | 4th | 3 | 42 | 7.5 | 18.5–20 | 0.347 | 0.220† | 2.7 |
| 28 T | 1st | 4 | 40 | 7.5 | 19.5–20.5 | 0.511 | 0.341 | 4.7 |
| 49 T | 6th | 4 | 40 | 7.5 | 20–21 | 0.551 | 0.364 | 5.1 |
| 24 P* | 1st | 4 | 40 | 7.5 | 19–21 | 0.432 | 0.280 | 3.9 |
| 25 P | 1st | 4 | 40 | 7.5 | 18–20.5 | 0.437 | 0.285 | 4.0 |
| 50 P | 2nd | 4 | 40 | 7.5 | 20–21 | 0.427 | 0.276 | 3.8 |
| 51 P | 3rd | 4 | 40 | 7.5 | 20–21.5 | 0.437 | 0.285 | 4.0 |
| 52 P | 3rd | 4 | 40 | 7.5 | 19.5–21 | 0.424 | 0.282 | 3.9 |
| 53 P | 4th | 4 | 40 | 7.5 | 20–21 | 0.427 | 0.284 | 4.0 |
| 26 P | 1st | 4 | 40 | 9 | 19–21 | 0.416 | 0.288 | 4.1 |
| 54 P | 2nd | 4 | 40 | 9 | 20–21.5 | 0.422 | 0.286 | 4.0 |

* Technical chloride=T; pure=P.
† Average for two membranes only.
‡ Note effect of low temperature.

five or six times does not increase variation in membranes appreciably.

In all the experiments here reported no covering of any kind was placed above the calcium chloride in its container. Twice, however, in experiments not reported, 0.1 gm. absorbent cotton was placed in the top of the chloride container with the result that a $G_w$ of about 4 was obtained where one of 2 was otherwise to be expected.

Neither was any attempt made to test temperature effects carefully but in several cases not reported the temperature fell, during the night, to about 15° C. These membranes were markedly heavier than similar ones prepared at about 20°, although for more than half of the evaporation period the temperature for these also had been near to 20°. In other cases there were variations among the four membranes prepared at one time which variations could be accounted for in no other way than by supposing the temperature of the evaporation chamber had been uneven.

The data reported above, gathered for the purposes stated, also make possible a somewhat inadequate comparison of membranes as to reproducibility from day to day. From the results of these investigations extending over a period of six months and involving the preparation of more than 70 sets of four membranes each,—54 sets being reported herewith,—the writer considers that average variation from one set to another should be less than 5%, provided temperature and other conditions are as constant as those used in the present work. Within the group of four membranes prepared at one time the agreement should be closer. The following figures for wet weights of the membranes in two sets may be considered typical of the best agreement that may be expected: 0.145, 0.147, 0.146, 0.146; and 0.199, 0.197, 0.195, 0.196. Extreme variations of as much as 15 milligrams in the wet weights of the four membranes were rare and were probably due to uneven temperature, or, if they concerned one membrane only, to contamination or gross error in weighing. In the former case the

set was rejected or duplicated, and in the latter the membrane rejected.

A comparison of the "weights before washing" for the whole series of membranes with the average wet weights for each set (of four membranes) shows the agreement to be good and thus furnishes corroboration of the findings of Nelson and Morgan.[13] (See Figures 2 and 4). When weighed cov-

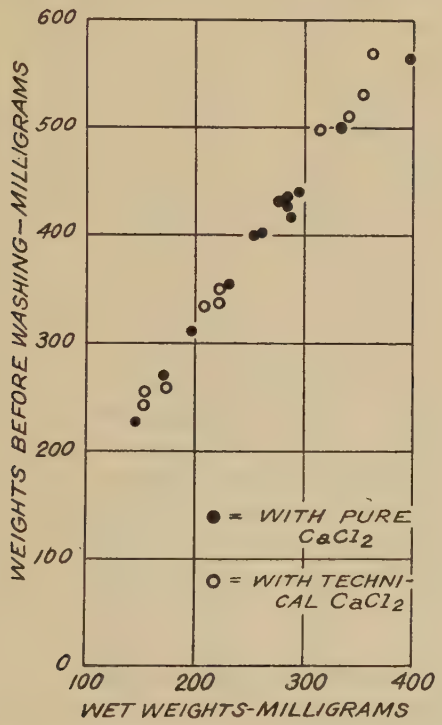


Fig. 4. Wet weights of membranes in relationship to the weights of the same membranes before washing.
Data summarized from all tables.

ered the loss while weighing a film on its glass plate does not exceed a milligram or two and is possibly more accurate than is the wet weight. This is therefore another quick and easy method for comparing films and has the advantage over wet weights of not being likely to damage the membrane.

## CONCLUSIONS.

From all the observations in connection with the present investigation as well as from the data here presented the writer considers the method proposed by Pierce[9] for grading collodion membranes by means of ethylene glycol to be, in practice, a good and usable method. The chief difficulty probably concerns temperature control, but, as has been shown in the previous pages, if temperature is kept within a range of 19-21° C. the effect of the variations is negligible unless great precision is required.

A perfect gradation of membranes in integral steps corresponding to the percentage of ethylene glycol in the nitrocellulose solution is not to be expected, since the glycol is appreciably volatile under the conditions of the experiment.

In order to describe adequately the making of a given membrane so that it may be reproduced it is necessary to specify: (1) the grade or quality of calcium chloride used in the container below the evaporation chamber; (2) the diameter of the opening between the chamber and the calcium chloride below; (3) the distance from the floor of the chamber to the unobstructed surface of the chloride; in addition to (4) air rate, temperature, and evaporation time, as with other methods. In the present work, using the apparatus previously described, the most satisfactory membranes appeared to be produced when pure calcined calcium chloride was used at a distance of 7.5 to 9 cm. below the floor of the evaporation chamber, the opening in the floor being 40 mm., the time 24 hours, the temperature 20° ± 1° C., and the air rate uniform at 22 ± 1 liters for 24 hours.

Weights of membranes (covered) on the glass plates, previous to washing, are functions of the wet weights of the same membranes.

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